Investigation of ion-pairing phenomenon in BaF$_2$ aqueous solution: Experimental and theoretical studies

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The ion-pair association constant values, related to the reaction Ba$^{2+}$ + F$^{-}$ \rightleftharpoons [BaF]$^+$, are determined by means of NMR spectroscopy. The values for thermodynamic functions of the ion-pairing process are calculated on the basis of the NMR results. In addition, the association entropy has been found to depend on temperature. Comparing the experimental data and Fuoss theory, it is found that [BaF]$^+$ contact ion-pair is formed in the BaF$_2$ aqueous solution. Also, hydration of barium-fluoride ion-pair is investigated by the DFT method. The hydration number of barium-fluoride ion-pair is determined by comparing the experimental and theoretical results. The effect of number of water molecules on the properties of ion-pairs is investigated by determining NQR and NMR parameters. Also, the relation between the chemical shifts and the energy gap between the highest occupied molecular orbital (HOMO) and low-lying virtual molecular orbital (LUMO) is investigated.

1. Introduction

In the Debye–Hückel theory, it is assumed that strong electrolytes completely dissociate in aqueous solution [1]. However, there is also much evidence to show that cations and anions in solution can associate to form ion-pairs, as a result of strong electrostatic attraction. In ionic compounds, the separation to ions is complete. However, if ions associate in solution, the dissociation is not complete. Small ion dimensions, high ion valence, and small solvent dielectric constants are conducive to ion-pair formation.

Hydration of ion-pairs is an essential process in the solvation of ionic crystals into water, chemical reactions in aqueous solution, and stability and functionality of biological systems [2–4]. Solvation effects can profoundly alter chemical and physical interactions.

The investigations show that dissolved ions in water have “structure making” or “structure breaking” effects on water, depending on the ion size and whether they are cations or anions [5]. For example, halide ions larger than Cl$^-$, i.e. Br$^-$ and I$^-$, are regarded as water structure breakers, while smaller ions such as F$^-$ are regarded as water structure makers. Yet it could equally be argued that a smaller ion, with its much greater local charge density, would be more likely to pull the water away from its hydrogen bonded configuration in the liquid than a larger ion, thus breaking the water structure [6,7]. Hribar et al. concluded that “small ions have high charge densities, so they cause strong electrostatic ordering of nearby water molecules, breaking hydrogen bonds” [7]. In other words, an ion which breaks water hydrogen bonds is regarded as a structure maker.

The ion-pairs were classified on the basis of mutual geometry of the ions and the solvent according to: (1) solvent-separated ion-pairs, (2) solvent-shared ion-pairs and (3) contact ion-pairs [8].

Several methods of studying ion-pairing including conductivity methods [9–15], ion-selective electrode potentiometry [16], gravimetric, solvent evaporation [17], NMR spectroscopy [18–22], and theoretical modeling [23–26] have been used to probe the phenomenon of ion association in both aqueous and non-aqueous solvents. Theoretical methods like DFT assume some structures in the solution and only a correct assumption leads to a theoretical result that agrees with experimental results. Thus, such agreement indicates indirectly the structure of the molecules. For example, the experimental and theoretical studies have been shown that Mg$^{2+}$ is coordinated by six water molecules in an octahedral arrangement [27]. Also, the DFT and experimental $^{19}$F NMR chemical shifts for sulfur-containing compounds have been shown